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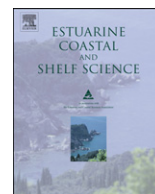
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Inter-annual variability of CO₂ exchanges between an emersed tidal flat and the atmosphere

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ABSTRACT

Carbon dioxide (CO₂) exchanges between a tidal flat (Wadden Sea, Netherlands) and the atmosphere were measured during a three-year survey. CO₂ exchanges were monitored during 1–2 days each month between September 2006 and September 2009 using a flux chamber. The flux of CO₂ was separated into two fluxes: the dark flux and the gross light flux, with the dark flux representing the flux during darkness and the gross light flux the difference between the net CO₂ flux (measured under light) and the dark flux. It was argued that dark and light fluxes may deviate from respiration and photosynthesis, as the fluxes between wet tidal sediment and the atmosphere are affected by the partial pressure of CO₂ in pore water, which is only gradually changed by sources and sinks of CO₂ in the sediment. Light and dark fluxes were empirically related to environmental parameters in order to interpolate between succeeding measurements. The dark flux appeared to increase with temperature and the light flux became more intense with increasing irradiance with signs of saturation at high light levels on many but not all measurement days. These relations with environmental parameters showed seasonal and inter-annual variability. Fluxes were negligible just after the site was emersed and it took up to 3 h of emersion until fluxes were adapted to environmental conditions. Dark and light fluxes both showed strong seasonality with high values in summer and low values in winter. The tidal flat appeared as a source of atmospheric CO₂ in the first year of measurement (+0.35 mol CO₂ m⁻² yr⁻¹) and a sink in the following two years (–1.59 and –0.72 mol CO₂ m⁻² yr⁻¹). Since the source of CO₂ was observed during an extremely warm year, we suggest that climate warming might influence the carbon budget of tidal flats.

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1. Introduction

Global warming is, among other effects e.g. on biodiversity, expected to reduce the efficiency of the global carbon pump (Thomas et al., 2004; IPCC, 2007). During the last decades, reviews aimed to estimate the role of the open and the coastal ocean in the global carbon cycle (Heip et al., 1995; Frankignoulle et al., 1998; Gattuso et al., 1998; Thomas et al., 2005; Borges et al., 2006; Schiettecatte et al., 2007). Global CO₂ emission scenarios suggest that atmospheric CO₂ concentrations could reach 800 ppm by the end of the century (IPCC, 2007), which would have a critical impact on the biogeochemistry of the ocean. In this context, exchanges of CO₂ between the ocean and the atmosphere appear to be a key factor in

the global carbon budget and a description of the exchange processes is needed to determine the potential impact of anthropogenic CO₂ emissions. Over 40% of the carbon sequestration in the oceans occurs along continental margins (Muller-Karger et al., 2005), but CO₂ fluxes vary widely in these areas. For example, the North Sea is a sink for CO₂ (Thomas et al., 2005; Schiettecatte et al., 2007), whereas the surrounding estuaries of Elbe, Ems, Rhine and Scheldt act as sources of CO₂ (Frankignoulle et al., 1998; Borges et al., 2006).

The net direction of CO₂ exchanges is even more variable for intertidal sediments. This is explained by regional differences and the wide range of methods used. For example, flux chamber measurements showed both net CO₂ release (Migné et al., 2004, 2009; Spilmont et al., 2007) and net CO₂ uptake (Spilmont et al., 2005, 2006) at stations located along the French coast of the English Channel, and eddy-correlation measurements showed a strong uptake of CO₂ in spring by a tidal flat in the Wadden Sea (Zemmelink et al., 2009).

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Obviously, O_2 and CO_2 fluxes are interdependent, since CO_2 uptake and O_2 release are closely related during photosynthesis and respiration, although deviations between O_2 and CO_2 fluxes may arise from chemo-physical processes. The net yearly sign of O_2 flux is also still uncertain for tidal sediments in the Wadden Sea. Van Es (1982) measured a net yearly uptake of O_2 , suggesting a release of CO_2 , in 4 out of 6 stations located in the Dollard estuary where the river Ems flows into the Wadden Sea. Sandy sediments studied in the area have been characterized both by a yearlong net release (Asmus et al., 1998) or uptake of O_2 (Kristensen et al., 1997), whereas muddy sediments were described as net sinks for O_2 (Kristensen et al., 1997; Asmus et al., 1998). These previous results on CO_2 and O_2 exchanges on tidal flats suggest that sediment structure and composition may influence net exchanges and that the trophic status of tidal sediments is not determined yet. Thus, more measurements are needed to determine whether, or when and where tidal flats are a source or sink of atmospheric CO_2 . More specifically, multi-annual surveys are needed to estimate the inter-annual variability of the net exchanges, since existing data rely on relatively short lasting studies (i.e. less than two years). In this context, a site, remote from major river outflows, in the Dutch Wadden Sea was selected for the present study. The CO_2 flux chamber technique was selected as a direct method to reach the goal of a better understanding of the fate of atmospheric CO_2 in intertidal sediments and how it could be expected to develop in the context of global warming.

2. Site description

Tidal flats, generally several hundreds of meters wide are found along the coast of the Netherlands and the adjacent Wadden Sea. For the present study, one of these coastal tidal flats was selected that was situated close to the Lutjewad research station (Neubert et al., 2005) to get nearby meteorological data. The tidal flat ($53^\circ 24' 48''$ N, $6^\circ 20' 40''$ E; Fig. 1) was remote from major river estuaries: The Ems estuary was located only 30 km to East but water of the Ems flows away from the measurement location and into the German Wadden Sea and North Sea. Most of the flat consisted of a muddy surface of a few centimeters thick topping a sandy underground. At 3–5 cm depth, a black layer was common that was attributed to sulfate reduction by anaerobic mineralization. The surface was gray to brown with the brown glow attributed to the presence of diatoms (e.g. McIntyre et al., 1996). The intensity of the brown glow varied temporally between succeeding measurement days and spatially with most brown spots near the shoreline of high

tide. Measurements were mostly taken seawards of the brown spot area at several locations in an area that visually appeared as representative for large parts of coastal tidal flats in this part of the Wadden Sea. Mean annual temperature in the period 1981–2010 was 9.5°C with a range from 2.8°C in January and February to 17.0°C in July and August (<http://www.klimaatatlas.nl>); mean tidal range was 2.4 m (http://live.getij.nl/getij_resultaat.cfm?location=LAUWOG).

3. Methods

3.1. CO_2 flux measurement

Exchanges of CO_2 between the atmosphere and the tidal flat were measured during emersion (low tide) using the flux chamber method (Migné et al., 2002). Dimensions of the chamber were 0.25×0.25 m and 0.15 m height. The chamber was made of UV transmitting Polymethylmethacrylate. Within the flux chamber, CO_2 concentration and air temperature were measured using a Vaisala GMP343 open path analyzer. The instrument was calibrated regularly in the laboratory on CO_2 concentrations of 0 and 507 ppm. The calibration showed good long-term stability. However, some drift occurred in the first half hour of use, so field measurements started half an hour after turning the instrument on. Measurements of CO_2 exchange took place once or twice a month from September 2006 to September 2009, giving a total of 51 measurement days. Measurements were made at variable times between an hour before sunrise until an hour after sunset.

The flux of CO_2 was separated in two components: the dark flux and the gross light flux, with dark flux representing the CO_2 flux during darkness and gross light flux the difference between net light CO_2 flux (i.e. the CO_2 flux measured under light) and simulated dark flux at observed temperature. The light flux was thus considered as showing the impact of irradiance alone on CO_2 fluxes. Dark flux was measured on 14 out of 51 measurement days during natural darkness, generally during the last hour of the night before sunrise. Dark flux was also measured during artificial darkness at daytime using a light blocking flux chamber. The chamber was placed at least 1.5 h prior to measurements for adaptation of quick and slow processes to darkness. A limitation of the chamber technique is that boundary conditions may deviate from the surrounding; some cooling of the sediment in the dark flux chamber was observed due to prolonged light blocking, and measurements were corrected for this effect. The dark flux chamber was flushed with outside air to keep CO_2 concentration within

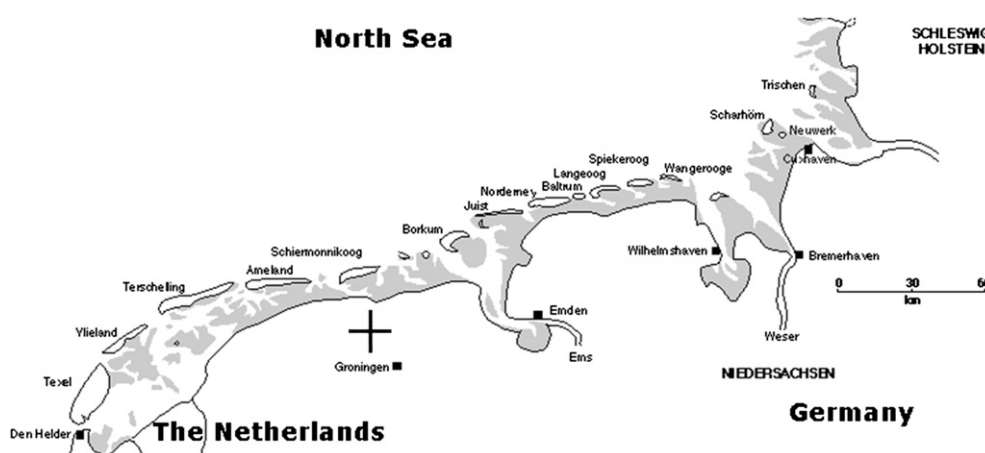


Fig. 1. Map of the Wadden Sea showing the study area (cross). Gray colors represent tidal flats.

1 ppm of the surrounding air during the period that the sediment adapted to darkness.

The CO₂ concentration started to change as soon as the transparent flux chamber was placed on the sediment or flushing of air through the light-blocking chamber was stopped. The CO₂ flux was calculated from the rate of CO₂ change with time. In situations of CO₂ release, a linear increase of CO₂ concentration with time was observed with some measurement noise superimposed. The rate of change was then calculated from a linear fit to the data. In case of CO₂ uptake, on the other hand, the uptake rate was found to decrease slowly with time. A good fit to the data was found by an exponential equation, implying that CO₂ uptake rate was proportional to CO₂ concentration in the flux chamber. The flux was then calculated from the initial gradient of the exponential fit. A flux in upward direction, from sediment to atmosphere, was defined as positive. The accuracy of a measurement increased with measurement time due to instrumental noise. A 2-min time resulted in 5% measurement uncertainty, and uncertainty in a 5 min time was well below uncertainty arising from variable boundary conditions. Errors from instrumental noise are random and are negligible, compared to the random error, resulting from the 800 m distance between tidal flat and location of the radiation measurement. Although a measurement time of 5 min was appropriate for an accurate flux calculation, an almost two times longer period was commonly used to check measurements on irregularities that occasionally appeared from variations in irradiation or leakage of outside air into the flux chamber.

3.2. Measurement of environmental parameters

Meteorological data were obtained from the Lutjewad research tower (Neubert et al., 2005), located 0.8 km south of the tidal flat. Global radiation was measured using a Kipp CMA pyranometer and air temperature at 7 m height using PT100 resistors. The pyranometer measured R_g, the incoming global radiation of the full solar spectrum. Note that the relation between R_g (W m⁻²) and photosynthetic active radiation PAR (μmol m⁻² s⁻¹) under clear sky conditions averages as (Jacovides et al., 2007):

$$\text{PAR} = 1.99R_g \quad (1)$$

Temperature of the top layer of the sediment was measured at several locations inside and just outside the flux chambers using commercial available digital pen thermometers that were calibrated at 0.1 °C accuracy in the laboratory to determine a possible impact of the flux chamber on sediment temperature. The tidal cycle consisted of about 3 h of submersion. The period of submersion was determined from tidal cycle data of station Lauwersmeer, located 10 km west of the tidal flat and available from www.getij.nl.

3.3. Calculation of yearly exchange

Dark and light fluxes were related to environmental parameters: temperature, irradiation and tidal phase for each measurement day. Dark flux D (μmol CO₂ m⁻² s⁻¹) was related to temperature T (°C) according to Parsons et al. (1995):

$$D = a \exp(b T) \quad (2)$$

The factor 'a' is described as 'dark flux factor'. The value of b is related to Q_{10} according to e.g. Gillooly et al. (2001):

$$Q_{10} = \exp(10 b) \quad (3)$$

where Q_{10} is the factor of dark flux increase when temperature increased by 10 °C.

Light flux L (μmol CO₂ m⁻² s⁻¹) was related to global radiation R_g according to Webb et al. (1974):

$$L = -c(1 - \exp(R_g/d)) \quad (4)$$

where c is the maximal CO₂ flux under light saturation and d is generally called I_k , that is the saturation onset parameter.

Dark and light fluxes were calculated with an increment of 0.5 h during the three-year period from Eqs. (2) and (4) using meteorological and tidal data. The variables: a , b , c and d in Eqs. (2) and (4) were interpolated between succeeding measurement days in the following way: A fixed value of b was used for the three-year observation period as on most measurement days the variation of temperature was too small to statistically determine significant variations of b between measurement days. The variable a was linearly interpolated between measurement days. Interpolation of the variables c and d was more complicated, because several measurements did not show any sign of saturation, implying infinite large values for c and d . Finite values are needed to get a smooth interpolation between succeeding measurement days; Smooth interpolation was obtained by linear interpolation of c/d and $1/d$ instead. These variables describe the following processes: The variable c/d describes the sensitivity of light flux to global radiation for low values of irradiance when saturation is not yet effective and will be denoted as 'low light efficiency'; the variable $1/d$: 'light saturation factor' describes the intensity of saturation: lack of saturation implies $1/d = 0$. Several measurements of organic matter and chlorophyll a were made, but were not used in the analysis because of poor correlations with light and dark fluxes. Instead, this study was based on environmental parameters that were measured all year round and could thus be used for interpolation.

The impact of the tidal phase was taken into account by setting exchanges with the atmosphere $D = L = 0$ during submersion (high tide) when a layer of water prevented direct exchange between sediment and atmosphere. The neglect of exchange during submersion implies that this study was restricted to emersion. Light and dark fluxes were gradually increasing the first 3 h after the start of emersion, as shown in Section 4.3 and explained in section 5. The gradual increase was simulated by multiplication of D and L with a factor that increased linearly from 0 at the start of emersion to 1 after 3 h after the start of emersion (see Fig. 6).

4. Results

4.1. Dark fluxes

Dark fluxes during real darkness were often performed at lower temperatures than dark fluxes under artificial darkness (Fig. 2) as night temperature tended to be below daytime temperature. A single exponential curve fitted all dark flux measurements adequately: $D = 0.0495 e^{0.113 T}$, $n = 99$, $R^2 = 0.66$. The exponential factor resulted in $Q_{10} = 3.1$. The scatter around the exponential fit was not random as on some days all dark fluxes were well below or above the fit. These deviations were described with the dark flux factor a that showed seasonal and yearly variability with generally high values in summer and low values in winter and low values in the year 2008 (Fig. 3). Sediment temperature in the dark flux chamber was up to 2 °C below the surrounding during daytime due to prolonged shielding of the sediment from light. Fluxes were corrected for this effect using Eq. (2).

4.2. Light fluxes

Light fluxes showed significant scatter when plotted versus irradiance (Fig. 4). Light fluxes approached to a minimum negative

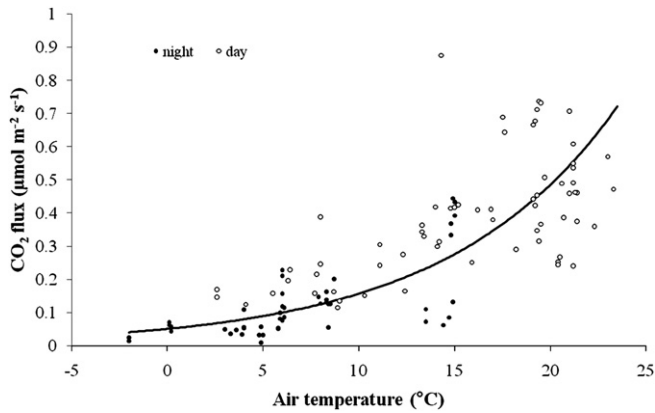


Fig. 2. Dark fluxes ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) versus temperature ($^{\circ}\text{C}$) for measurements performed during real (night, black dots) and artificial (day, open dots) darkness and exponential equation fitted on the data ($D = 0.0495 e^{0.113 T}$, $n = 99$, $R^2 = 0.66$).

value for high irradiation on most days, but 13 out of 51 measurement days did not show any limitation, implying $1/d = 0$. Lack of limitation did not result from low values of global radiation during that day but was instead commonly observed on sunny days when irradiation was large enough to expect saturation in the uptake rate of CO_2 by microphytobenthos. Measurement uncertainties could not explain the surprising lack of saturation of CO_2 flux at high irradiation, because of the large (13) number of days where saturation was not observed.

Low light efficiency 'c/d' and light saturation factor '1/d' both tended to be larger in winter than in summer (Fig. 5).

4.3. Tidal phase

Exchanges of CO_2 were negligible at the start of emersion and increased slowly until maximum values were measured after 3 h of emersion (Fig. 6). Note that the slow build up is observed for light fluxes as well as for dark fluxes. Dark flux should also increase if sediment temperature had increased after emersion, but sediment temperature, like air temperature, appeared to stay constant within 1°C during the measurement period of Fig. 6, expect for some cooling during the last half hour. A time lag of 3 h to obtain full fluxes after the start of emersion was observed on several measurement days; 28 August 2007 was selected as an example because variations in temperature and irradiance were limited during the first hours of emersion. Dark and light fluxes did not show any sign of change near the end of the period of emersion.

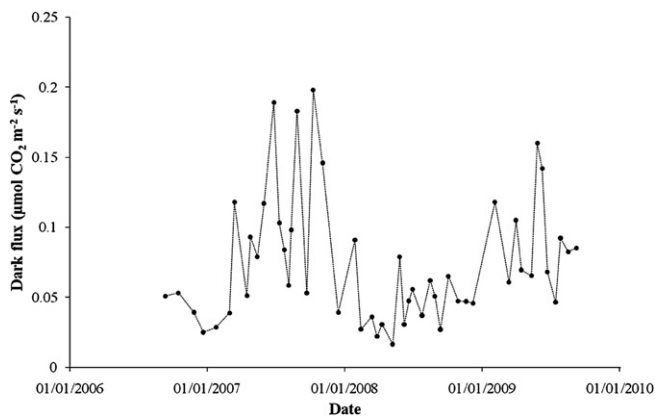


Fig. 3. Development of the dark flux factor ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) over three years of measurements.

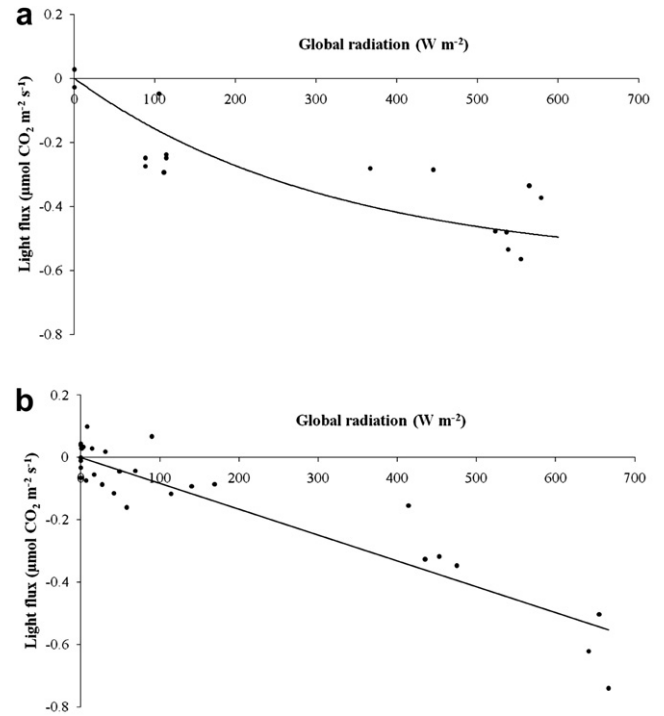


Fig. 4. Light fluxes ($\mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$) versus global radiation (W m^{-2}) on a) 27 May when saturation at high irradiation was clearly observed ($L = 0.584 [1 - e^{-0.00315 R_g}]$, $n = 16$, $R^2 = 0.70$). b) 8 May without any sign of saturation ($L = -0.00083 R_g$, $n = 29$, $R^2 = 0.86$).

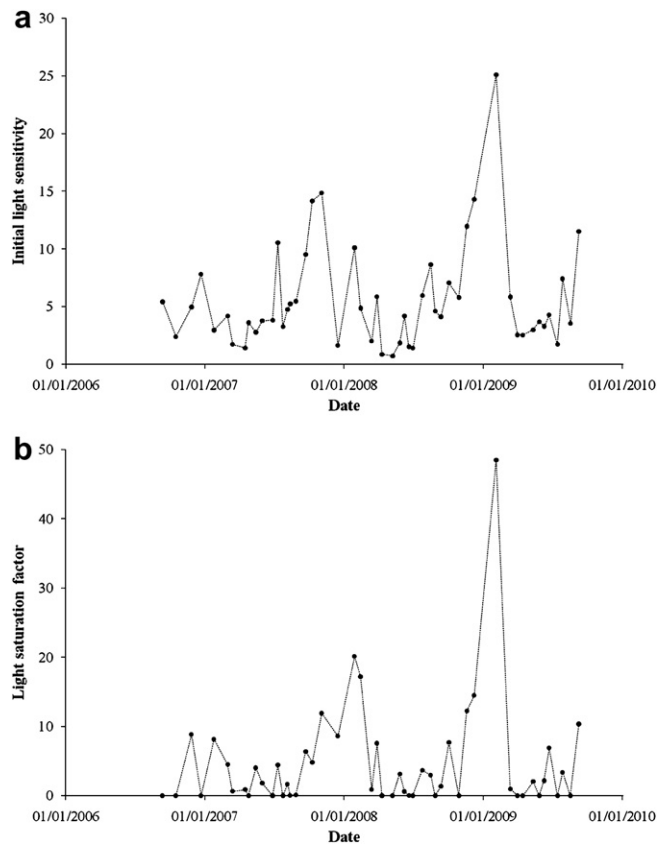


Fig. 5. Development of a) Low light efficiency ($\mu\text{mol CO}_2 \text{ W}^{-1} \text{ s}^{-1}$) and b) Light saturation factor ($\text{m}^2 \text{ W}^{-1}$) during the three years of measurements.

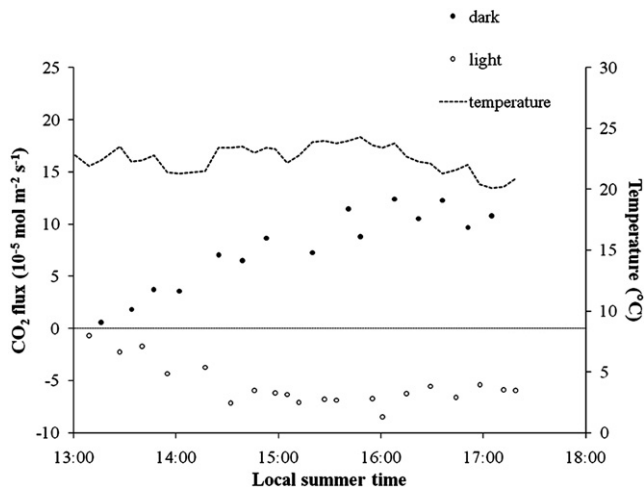


Fig. 6. Light fluxes ($10^{-5} \text{ mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, open dots), dark fluxes ($10^{-5} \text{ mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$, black dots) and temperature ($^{\circ}\text{C}$, dashed line) on August 28, 2007 versus time of day. At 13:00 h a thin layer of water was the last remains of high tide. Pores of the sediment were saturated with water during the first hours of emersion.

4.4. Inter-annual variability

The start of the year was set at 15 September as measurements started in September 2006 and ended in September 2009, so autumn stands for the period from 15 September to 15 December and similarly for the following seasons (Fig. 7). Dark and light fluxes appeared of similar magnitude as both showed maxima in summer and minima in winter. Fluxes were negligible on cold winter days when ice impeded CO_2 exchange and fluxes in excess of $1 \mu\text{mol CO}_2 \text{ m}^{-2} \text{ s}^{-1}$ were observed several times on warm summer days. Some differences between the magnitude of light and dark fluxes were obvious: Light flux was below dark flux in all winters and light flux exceeded dark flux in summer 2008. Total fluxes were defined as the sum of light and dark fluxes; a positive value means that the tidal flat was a source of atmospheric CO_2 . Dark flux exceeded light flux during the first warm year of measurements (Table 1), whereas in the following years with more normal temperatures, the tidal flat appeared as a sink for atmospheric CO_2 .

5. Discussion

The brown glow of the sediment indicated the presence of algae in and on the sediment. Biological processes could explain most of the results: the increase of dark fluxes with temperature agreed with the expectation of an increase in respiration, and the intensification (more negative) of light fluxes with increasing irradiance and temperature agreed with an expected increase of photosynthesis, both at day and seasonal scales. Low light efficiency and light saturation factor were both relatively large during winter and during cloudy days, suggesting adaptation to light regime in a way that in periods of limited light availability the benthic organisms use small irradiance more efficient at the cost of stronger limitation at higher light intensities (e.g. Migné et al., 2004).

However, not all results could be explained from biological processes. Saturation at high irradiance was absent on many days, in particular during sunny days. As physiological processes would lead to saturation in the uptake rate of CO_2 by algae, more processes than only physiology must be involved in the exchange of CO_2 at the sediment–atmosphere interface. Also, the slow build up of dark flux after the onset of emersion is hard to understand from physiology in the situation where sediment temperature was almost constant.

Fluxes of CO_2 between atmosphere and sediment are also affected by the partial pressure of CO_2 (pCO_2) in the pore water of the sediment. The pCO_2 depends on the amount of dissolved inorganic carbon (DIC, the sum of CO_2 , HCO_3^- and CO_3^{2-}) in the water, as well as on temperature, alkalinity and, to a lesser amount, salinity of the pore water. So, physiological processes affect DIC in the pore water and indirectly pCO_2 and CO_2 flux to the atmosphere. These chemo-physical properties were not constant during measurement days; it was visually observed that the pore water content was highly variable. Changes in pore water might possibly explain the observed lack of saturation in the following way: evaporation depends on light and results in concentration of the remaining pore water and could thereby result in a further decrease of pCO_2 and enhancement of CO_2 flux to the sediment. So, we hypothesize that flux enhancement at high irradiation following evaporation of pore water may compensate physiological saturation and explain the observed lack of saturation in CO_2 fluxes on many sunny days. Further research is recommended to quantify the influence of chemo-physical processes in pore water on CO_2 fluxes at the interface of sediment and atmosphere.

The sensitivity of CO_2 exchange between sediment and atmosphere to pCO_2 may explain the behavior of light and dark fluxes during the first hours of emersion in the following way: during submersion, pore water of the sediment may exchange with overflowing water. Anaerobic degradation of organic matter in the sediment during submersion, followed by exchange with seawater may increase alkalinity and CO_2 buffer capacity of seawater (Thomas et al., 2009). Exchange with seawater during submersion should drive the concentration of pCO_2 in pore water of the sediment close to equilibrium with seawater. The pCO_2 of seawater in the North Sea is in close equilibrium with the atmosphere (e.g. Thomas et al., 2005) and this may explain the small light and dark fluxes at the very beginning of emersion. Processes like photosynthesis and respiration in the sediment would gradually change DIC in pore water during emersion, and thereby slowly changing pCO_2 and the flux of CO_2 between tidal sediment and atmosphere. This process may explain why both light and dark fluxes increased slowly and with the same time constant after the start of emersion. Microphytobenthos migration (Consalvey et al., 2004) may also result in a slow increase of light fluxes after the start of emersion but an effect on dark fluxes is less obvious. A time lag of 3 h to build up light fluxes after the onset of emersion was also observed by Spilmont et al. (2007), meaning that a slow response of CO_2 flux to forcing is common for wet tidal sediment. However, Spilmont et al. (2007) argued that this result was only due to microphytobenthos vertical migration to prevent from photo-inhibition and/or re-suspension. Here, we stress that chemical processes related to DIC and pCO_2 in pore water should be involved to understand exchange of CO_2 fluxes between wet sediment and the atmosphere. Solubility of CO_2 suggest that a few centimeters of pore water in the upper sediment are needed to explain the slow reaction of CO_2 fluxes to changes in environmental conditions, but more data on pore water content and composition are needed for quantitative results.

Light and dark fluxes were only calculated during emersion as this study is focused on exchange with the atmosphere. Respiration and photosynthesis do continue during submersion, but CO_2 is then exchanged with the water column instead of directly to the atmosphere. By focusing on exchange with the atmosphere, this study does not itself inform on the trophic state of the tidal flat. To determine the trophic state of a tidal flat from CO_2 measurements, the measurements should be extended to the periods of submersion.

The scatter of light fluxes versus global radiation (Fig. 4) had at least two causes: First of all, measurements were made on different locations on the tidal flat, so scatter revealed spatial variability of

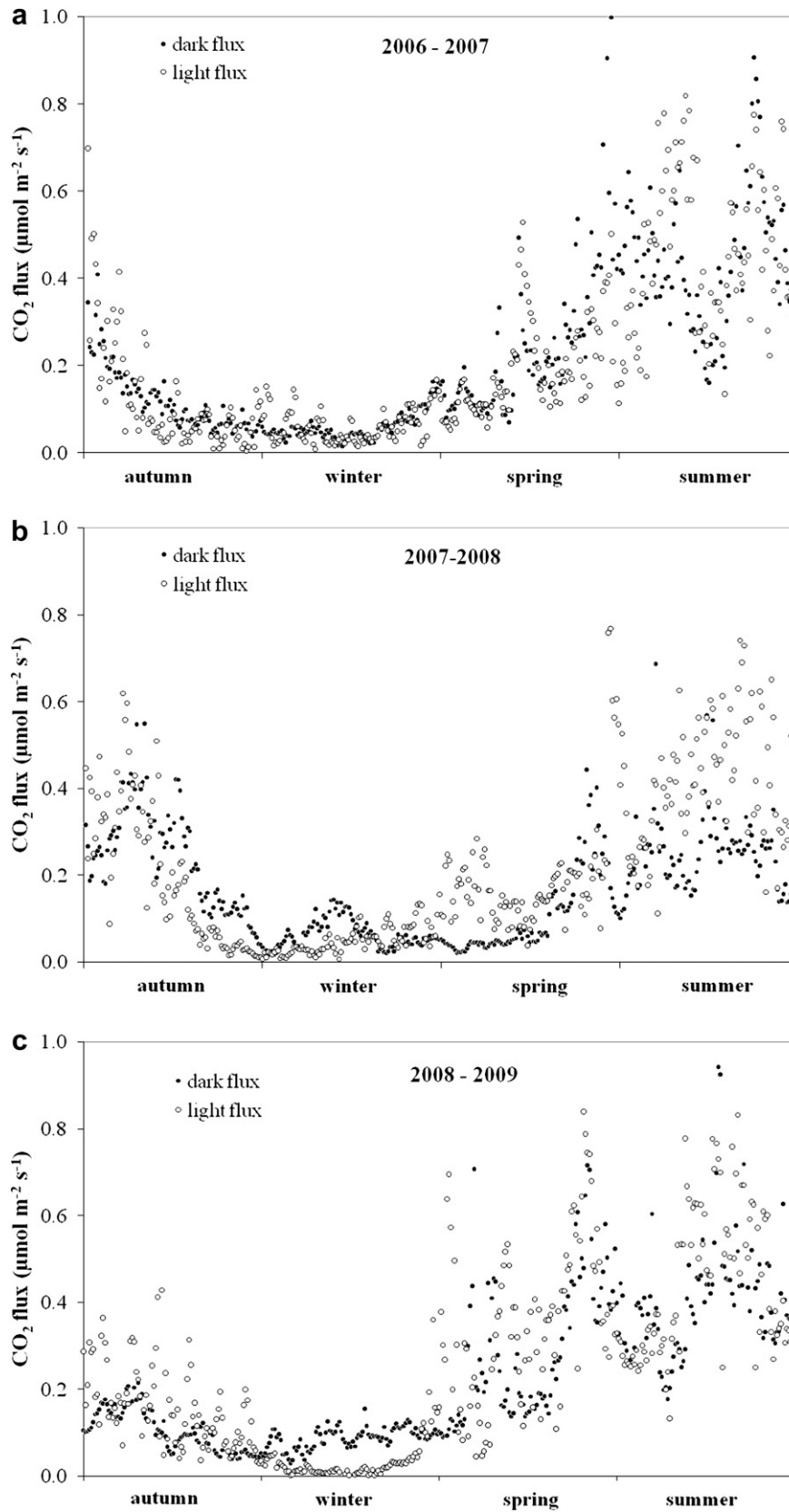


Fig. 7. Development of light fluxes (μmol CO₂ m⁻² s⁻¹, open dots) and dark fluxes (μmol CO₂ m⁻² s⁻¹, black dots) over the three years of measurements (a: 2006–2007, b: 2007–2008 and c: 2008–2009).

Table 1

Year average fluxes, temperature and irradiance for the three year survey conducted on the Wadden Sea tidal flat.

Year	Dark flux (mol m ⁻² yr ⁻¹)	Light flux (mol m ⁻² yr ⁻¹)	Total flux (mol m ⁻² yr ⁻¹)	Temperature (°C)	Irradiance (W m ⁻²)
2006 –7	+7.0	–6.7	+0.35	11.6	118
2007 –8	+5.2	–6.8	–1.59	10.3	116
2008 –9	+7.1	–7.8	–0.72	9.7	120

flux over the tidal flat, but it also resulted in integration of spatial variability to get a better estimate of spatially averaged CO₂ exchange. Irradiance measurements were executed 0.8 km away from the flux measurements and this distance could be another cause of scatter in the light flux curve, especially on days with scattered clouds.

Inter-annual variability in CO₂ fluxes appeared too large to answer the question whether the tidal flat was a source or sink of atmospheric CO₂ from this study alone. The large inter-annual variability and the large area of tidal flats in the Wadden Sea may motivate further research on the carbon balance of tidal sediments, in particular long-term monitoring. The transition of the tidal flat from a source to a sink for atmospheric CO₂ between succeeding years came as a surprise. Inter-annual variability of global radiation was small during these years and measurements of nutrients and dissolved carbon in the water column at the inlet of water from the North Sea into the Wadden Sea at the Marsdiep near Den Helder were not significantly related to year average CO₂ fluxes at the tidal flat (Phillipart, personal communication). The Marsdiep location is far away from the tidal flat of the present study, but average flow of water is from the Marsdiep to the tidal flat. Irradiance and nutrients could not explain the transition between source and sink, but yearly CO₂ fluxes were clearly related to mean temperature: The tidal flat appeared as a source of atmospheric CO₂ during an exceptional warm year (<http://www.knmi.nl/klimatologie/>), and a sink during the following years when temperature was only slightly enhanced as compared to the 30 years climatic average temperature. This result raised the question whether climate warming should affect CO₂ exchange of tidal sediments, a question that cannot yet be answered with the limited number of years that measurements have been made at tidal flats.

6. Conclusion

Exchange of CO₂ between a tidal flat and the atmosphere was argued to depend not only on biological processes (i.e. related to respiration and photosynthesis), but also on chemo-physical processes of CO₂ in pore water of the sediment. Therefore a new terminology was needed to describe the processes of CO₂ exchange in darkness and the effect of light; the words 'dark flux' and 'light flux' are thus promoted. We recommend to include measurements of pore water content and –composition to quantify the effects of chemo-physical processes on CO₂ exchange at tidal flats.

Seasonality and relationship between light and dark fluxes were in line with previous studies. Even if, at the year scale, light and dark fluxes almost balanced each other, it can be significant for global carbon fluxes, given the extended surface covered by tidal flats. The tidal flat under consideration changed between a source and a sink of atmospheric CO₂ in following years and thus we underlined that a single year of measurements is not always sufficient to determine the sign of the year average CO₂ fluxes between the atmosphere and tidal flats; thus it appears critical to

extend research over several years. The present results also indicate that the tidal flat appeared as a source of atmospheric CO₂ during an exceptional warm year and as a sink during more normal years, which could be a warning that climate warming may affect the carbon balance of tidal sediments.

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